

The University of Chicago

CHANGES IN THE X-RAY DIFFRACTION PATTERN OF
NITROBENZENE PRODUCED BY AN ELECTRIC FIELD,
CHANGES IN TEMPERATURE AND CIRCULATION

A DISSERTATION SUBMITTED TO THE FACULTY OF THE
DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1933

By

FRANCIS CARTWRIGHT TODD

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
THE PHYSICAL REVIEW
Vol. 44, No. 10,
November 15, 1933

The University of Chicago

CHANGES IN THE X-RAY DIFFRACTION PATTERN OF
NITROBENZENE PRODUCED BY AN ELECTRIC FIELD,
CHANGES IN TEMPERATURE AND CIRCULATION

A DISSERTATION SUBMITTED TO THE FACULTY OF THE
DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1933

By

FRANCIS CARTWRIGHT TODD

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
THE PHYSICAL REVIEW
Vol. 44, No. 10,
November 15, 1933



Changes in the X-Ray Diffraction Pattern of Nitrobenzene Produced by an Electric Field, Changes in Temperature and Circulation

F. C. TODD, *Ryerson Physical Laboratory, University of Chicago*

(Received July 17, 1933)

Comparable diffraction patterns of benzene and nitrobenzene were taken with Mo *K* radiation. Two balanced, krypton-filled ionization chambers were arranged to read the difference in the ionization current produced by the x-rays diffracted at the same angle from two similar scattering samples. By their use, the change in the intensity of the nitrobenzene diffraction pattern due to a field of 10 kv per cm was found to be less than 0.3 percent over the entire principal peak. An average of 35 readings on the peak gave a change in intensity of -0.02 ± 0.06 percent.

These chambers were also used to measure the change in intensity of the diffraction pattern produced by (1) an increase in temperature from 16°C to 26°C, (2) an increase in temperature from 30°C to 42°C and (3) circulating the nitrobenzene past the point of illumination with x-rays at a velocity of 0.4 cm per second. These results were found to be in general agreement with the assumption that the nitrobenzene molecules associate in pairs and are dissociated by thermal or mechanical agitation.

INTRODUCTION

THE principal peak in the x-ray diffraction pattern of liquids is due to the interference between the separate molecules.¹ Any cause resulting in a more orderly arrangement of the molecules in the liquid will produce a sharpening of this peak and an increase in the maximum intensity of the peak. With a molecule having a permanent electric moment large in comparison with the moment induced by an electric field, such as nitrobenzene, an electric field will exert a force tending to cause the permanent electric moment of the molecule to line up in the direction of the field.² On the assumption of no interacting forces between the molecules, McFarlan³ estimated that the change in intensity of the

diffraction pattern due to any applicable electric field would, however, be too small to measure by ordinary methods. In checking his theory, McFarlan nevertheless found an increase in the intensity of the principal peak of the nitrobenzene diffraction pattern of 2.3 percent due to an electric field of 9 kv per cm. This contradiction of his simple theory led him to introduce a hypothesis concerning the motion of groups of molecules.

The purpose of this work was to investigate the basis for this hypothesis by determining the effect of an electric field on the entire nitrobenzene diffraction pattern. To complete the study, it was necessary to measure the effect of small changes in temperature and the effect of circulation on the nitrobenzene diffraction pattern. Some measurements on the effect of temperature have been previously reported.⁴

¹ P. Debye and H. Menke, *Ergebnisse der Technischen Röntgenkunde* 2, 1 (1931).

² R. D. Bennett, J. Frank. Inst. 211, 481 (1931).

³ R. L. McFarlan, *Phys. Rev.* 35, 1469-75 (1930).

⁴ G. W. Stewart, *Phys. Rev.* 39, 176A (1932).

The nitrobenzene molecule has a permanent electric moment of about 4.0×10^{-18} e.s. units. The permanent moment is not located in the NO_2 group alone; but this group is negative with respect to the benzene ring,⁵ as shown by the structural chemical formula in Fig. 1A. Recent x-ray studies of crystalline benzene indicate that

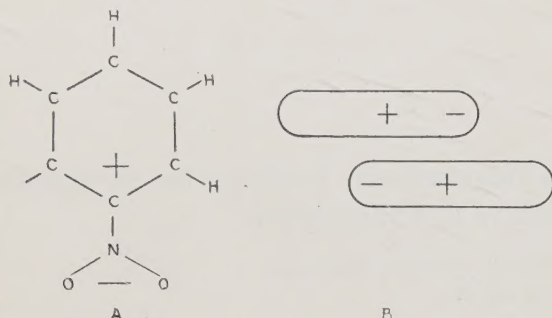


FIG. 1. The structural chemical formula of nitrobenzene.

the benzene molecule is flat⁶ with all the carbon atoms in a single plane. Smyth⁷ concludes from various evidence that the moment of the nitrobenzene molecule lies in the plane of the carbon atoms. This indicates that the nitrogen atom lies in the plane of the carbon atoms and that the oxygen atoms must be symmetrically placed with respect to this plane. Moreover, a comparison of the density and the atomic weights of nitrobenzene and benzene and a comparison of the x-ray diffraction patterns of these two liquids show that these are consistent with the hypothesis that the oxygen molecules also lie in the plane of the carbon atoms.

An explanation of the variation of the molar polarization of nitrobenzene with its concentration in a nonpolar solvent has been advanced which is based on the assumption that a certain fraction of the single molecules associate to form double molecules as shown in Fig. 1B.^{8, 9} In this type of association, the dipoles of the single molecules oppose and cancel each other. It must be remembered that nitrobenzene is not an asso-

ciated liquid¹⁰ in the same sense as water since there are no electron linkages or coordinate links between the molecules. Malsch,¹¹ from a theoretical basis, and Pal,⁸ by an empirical application, found that the number of dissociated molecules may be approximated by a relation of this type

$$N = N_0 e^{-U(x, y, z, \theta, \phi)/kT},$$

where U signifies the potential energy of the dipole, while k and T have their usual significance. By this relation the number of dissociated molecules increases as the temperature is increased. The dipoles of the dissociated molecules are, however, no longer neutralized and these dipoles will interact with the neighboring molecules. This increases the intermolecular forces as is indicated by the increase in viscosity with temperature.¹²

DESCRIPTION OF APPARATUS

The source of x-rays was a water-cooled Coolidge molybdenum target tube operated at 30 m.a. and approximately 35 kv peak by a full wave rectifier. The radiation was filtered by a ZrO filter to produce a more monochromatic radiation. The spectrum of the radiation is shown in Fig. 5. The x-ray tube and the rectifier were oil-immersed in the same tank, described in detail elsewhere.¹³ The electric circuit used was not the one there described, but will be explained in an early issue of *The Review of Scientific Instruments*. This circuit kept constant the intensity of the x-rays scattered at the principal peak of the benzene diffraction pattern, independently of changes in the line voltage. The circuit depends for its successful operation on the temperature of the x-ray tube filament changing as rapidly as the line voltage. Of course this is impossible; but this circuit does have a great advantage over those ordinarily employed. It was adjusted until a change of five percent in the line voltage produced a change of less than one percent in the intensity of the x-rays scattered at the benzene

⁵ I. Estermann, *Ergebnisse der Exakten Naturwissenschaften* 8, 303 (1929).

⁶ E. G. Cox, *Proc. Roy. Soc. (London)* A135, 491-8 (1932).

⁷ C. P. Smyth, *Dielectric Constant and Molecular Structure*, pp. 111-120.

⁸ N. N. Pal, *Phil. Mag.* 10, 265-80 (1930).

⁹ C. P. Smyth, reference 7, pp. 171-3.

¹⁰ N. V. Sidgwick, *The Electronic Theory of Valency*, p. 137.

¹¹ J. Malsch, *Phys. Zeits.* 33, 383 (1932).

¹² A. van Isterbeck, *Nature* 130, 399-400 (1932); Massy, Warren and Wolfenden, *J. Chem. Soc.* pp. 91-95 (1932).

¹³ Bennett, Gingrich, and Pierce, *Rev. Sci. Inst.* 2, 226 (1931).

peak. With this adjustment, the probable deviation of a single reading, as calculated from seventy readings, was 0.6 percent; and a plot of the deviations corresponded to an error curve. For the readings in this report, the line voltage was rechecked every few minutes to prevent its varying more than one percent from the mean. The points on the x-ray diffraction patterns for benzene and nitrobenzene in Fig. 6 indicate the steadiness of the circuit. All are single readings, except over the nitrobenzene peak where the points are averages of many readings. The curves approximate the average too closely to require correcting.

Although the probable deviation of the readings with this circuit is comparable with the best measurements on x-ray intensities, the accuracy is still insufficient to measure extremely small changes in intensity. To increase the accuracy, balanced ionization chambers were used, as shown schematically in Fig. 2. The vertical beam of x-rays from the tube was divided and passed through the two samples whose diffraction pat-

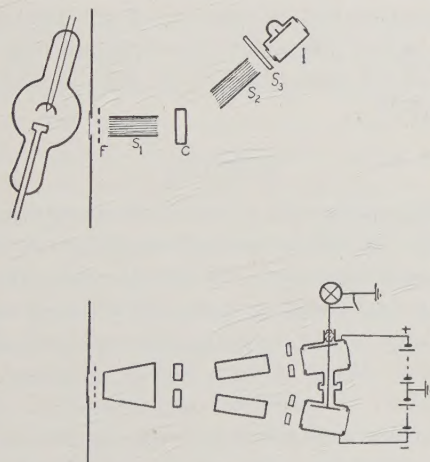


FIG. 2. Arrangement of apparatus for balanced readings of the ionization current. *F* is ZrO filter, *S*₁ and *S*₂ are Soller slits with slits 10 cm by 1 mm, *C* is scattering cell, *S*₃ is adjustable slit, *I* is the ionization chambers.

terns were to be compared. The two ionization chambers, mounted rigidly one above the other, were electrically connected to record the difference in ionization produced in the two chambers by the x-rays diffracted at the same angle from the two samples. This method has several advantages which increase the accuracy: (1) A change

in the x-ray intensity produces only a secondary effect on the difference. (2) The difference between two balanced readings with the scattering samples interchanged gives twice the effect to be measured. The scattering cells were not interchanged but the condition of the liquid inside the cells was changed. (3) Since the difference in intensity is recorded, a much more sensitive measuring device may be employed. (4) The ionization produced by stray radiation is practically balanced out over a reading of long duration.

The ionization chambers were carefully constructed to minimize the errors inherent in the measurement of very small currents. Krypton gas at 72 cm pressure was used in a copper walled ionization chamber. The length of the absorbing path through the krypton gas was 6 cm. All the precautions outlined by Compton¹⁴ for a similar chamber were carefully followed. The collecting electrodes are supported by two amber insulators, one in the electrometer and one in the ionization chambers. This reduces the chances for electrical leakage to a minimum, and the actually measured leakage was found to be very small. A Compton electrometer was used which had a sensitivity of 10,000 divisions per volt on a scale three meters distant.

The design of the circulating system for obtaining the effect of an electric field on the intensity of the diffraction pattern is shown in Fig. 3.

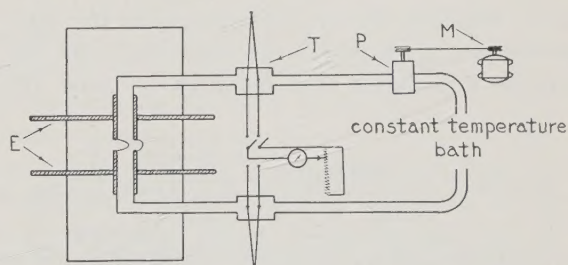


FIG. 3. Scattering cells and circulating system to determine effect of an electric field. *E* are the electrodes, *T* are thermocouples, *P* is the centrifugal pump and *M* is the synchronous motor.

The offset between the two cells produces the same state of turbulence in both. The thickness of the liquid in the scattering cell is 0.63 cm, approximately half the thickness for maximum

¹⁴ A. H. Compton, Rev. Sci. Inst. 2, 365 (1931).

scattering. Air chambers on each side of the cell prevent the condensation of moisture on the mica windows. The power for applying the field to the cell and to the x-ray tube was supplied by the same phase of the distribution system but each high voltage unit was otherwise separate. This insured that the peak of the x-ray intensity occurred at the time of peak voltage on the scattering cell. The voltage applied to the scattering cell was read by an electrostatic voltmeter, while the rectifier was supplying power. The nitrobenzene was circulated at a velocity sufficient to prevent an average temperature rise of more than 0.5°C due to the electric field in the scattering cell. The liquid was recooled to its initial temperature by circulation through a long coil of copper tubing immersed in a constant temperature bath. This method was so effective that no increase in temperature at the entrance to the scattering cell could be detected during a reading. The circulation was produced by a centrifugal type pump driven by a synchronous motor to prevent any pulsations in the flowing liquid. The temperature of the nitrobenzene was read at the points shown in Fig. 3 by the thermocouples, which were calibrated to read to 0.1°C .

The scattering cell and arrangement of apparatus for the study of the effect of temperature and to determine the effect of circulation are shown in Fig. 4. The upper and the lower scattering cells are independent of each other and may be joined to either of the two independent circulating systems. By thus interchanging the temperature of the liquid in the scattering cells, the difference between two readings is twice the

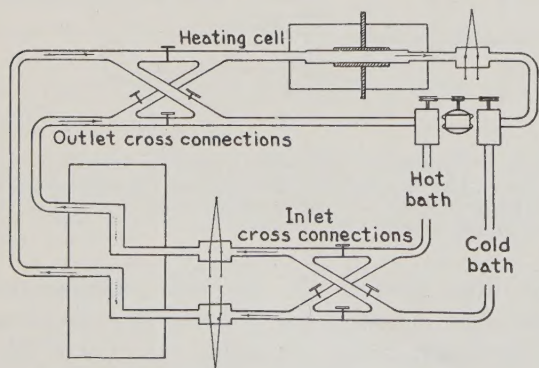


FIG. 4. Scattering cells and circulating system to study effect of temperature and circulation.

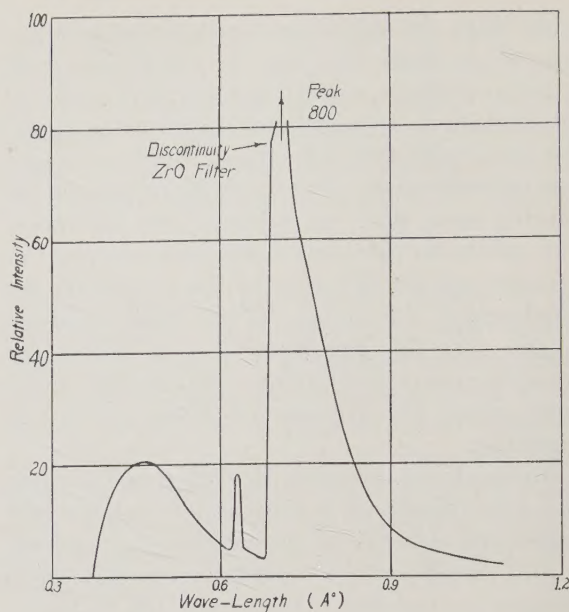


FIG. 5. Spectrum of radiation.

effect to be measured. The electrodes in the heating cell are connected to the same rectifier system as was used to find the effect of an electric field. By measuring the increase in temperature due to a given power input, the rate of circulation could be calculated from the specific heat of nitrobenzene, 0.34 .¹⁵

RESULTS

Fresh, commercial, c. p. nitrobenzene was used to obtain the diffraction pattern shown in Fig. 6. In the remaining tests, the nitrobenzene was used again several times as it discolored very slowly. It was kept in the circulating system only during the actual taking of data. While no precautions were taken to prevent contamination of the nitrobenzene with moisture from the atmosphere, all the materials with which the nitrobenzene came in contact were experimentally found to be dissolved inappreciably. In order partially to purify the nitrobenzene and to eliminate most of the anomalous conduction current, the nitrobenzene was circulated through the electric field for several minutes before each testing period.

The effect of an electric field of 10 kv per cm on the diffraction pattern is shown in Fig. 7. The readings for zero field were obtained to in-

¹⁵ Handbuch der Physik, Vol. X, p. 349.

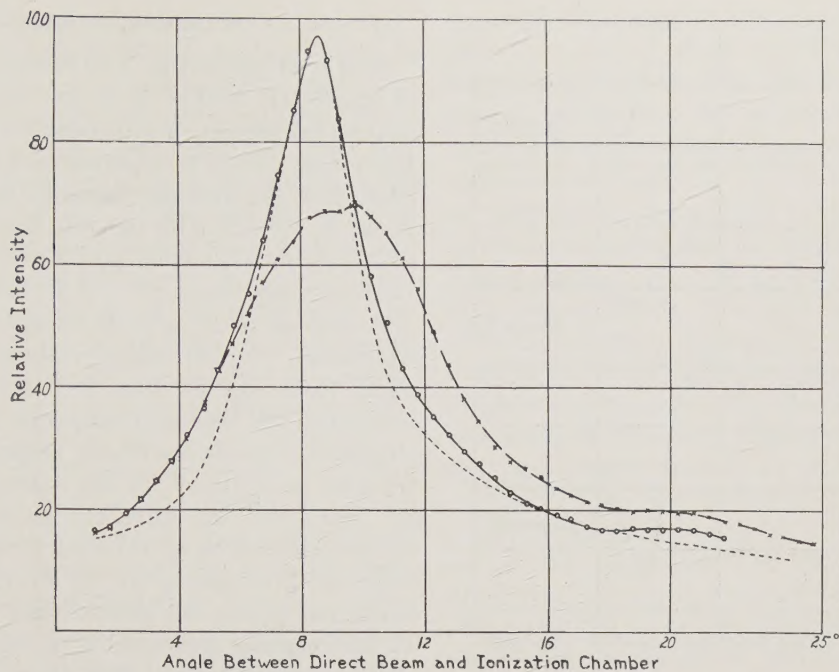


FIG. 6. X-ray diffraction patterns of liquids. Dotted curve is for benzene as given by Stewart, solid curve is for benzene, and dashed curve is for nitrobenzene.

sure that the circuit was not changing and when they varied too much the entire set was repeated. No corrections were made for the container scattering as the results apparently show no net effect. A group of 35 readings were taken at the angle of $8^{\circ} 30'$, each reading consisting of a drift rate with the field on the lower electrodes and another reading with the field on the upper electrodes. The average effect calculated from these readings was -0.02 ± 0.06 percent; that is, any effect due to the electric field is less than the precision of these experiments.

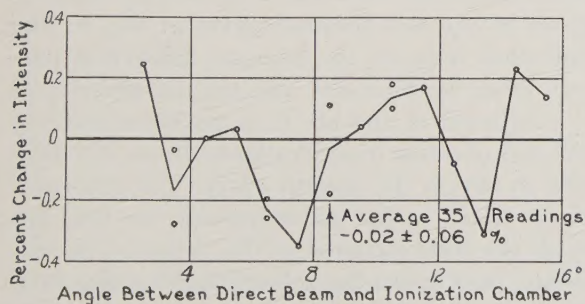


FIG. 7. Percent change in intensity of nitrobenzene diffraction pattern produced by an electric field. Strength of field 10 kv per cm, temperature of liquid 18°C and rate of circulation 0.5 cm per second.

The curves I and II in Fig. 8 show the effect of temperature on the nitrobenzene diffraction pattern. These curves give the change in intensity for several angles in percent of the total intensity diffracted at each angle. Curve I gives the increase in intensity produced by a 10°C increase in temperature from a reference temperature of 16°C . At still lower temperatures the readings were so irregular that a consistent group could not be obtained. Curve II similarly gives the increase in intensity produced by a 12°C increase in temperature from a reference temperature of 30°C . In this series of readings the nitrobenzene was not circulated while the readings were being taken; hence, no circulation effects are included. The dotted portions of the curves are not corrected for the container scattering. At these small angles, the fringing of the primary beam of x-rays plays an indeterminate rôle in the change of intensity. The readings showed a change in intensity of one x-ray beam relative to the other. This was traced to changing conditions in the oil surrounding the oil immersed x-ray tube and was partially eliminated. When the line voltage fluctuated rapidly, the readings were no longer so regular but varied over wide

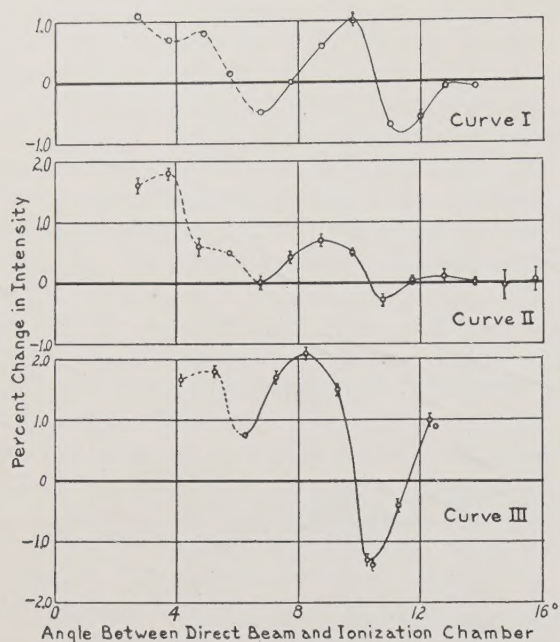


FIG. 8. Percent change in intensity of nitrobenzene diffraction pattern produced by temperature and circulation. Curve 1, increase in intensity produced by a 10°C increase in temperature from 16°C . Curve 2, increase in intensity produced by a 12°C increase in temperature from 30°C . Curve 3, change in intensity produced by circulating nitrobenzene at rate of 0.4 cm per second at a temperature of 23°C .

limits because of the characteristics of the circuit. To obtain the desired accuracy, readings were taken until a series of six, eight or more consecutive readings agreed. No points are given for which less than six readings were averaged.

Curve III in Fig. 8 presents the effect of circulating the nitrobenzene past the point of illumination by the x-rays at a velocity of 0.4 cm per second. The velocity was measured by the rise in temperature of the liquid for a given energy input as illustrated in Fig. 4. The existence of turbulence in the scattering cell was shown by the motion of air bubbles introduced into the circulating system. Turbulence was to be expected since the entrance and exit velocities of the liquid were three times that of the liquid in the cell. Nevertheless, the centrifugal pump circulated the liquid with sufficient steadiness to permit the reproducibility of the results shown in two readings, although these readings were taken several weeks apart.

DISCUSSION OF RESULTS

The readings in Fig. 7 to determine the effect of an electric field of 10 kv per cm on the x-ray diffraction pattern of nitrobenzene have no regularity that can be interpreted as a definite effect. Moreover, the average change in intensity at the peak of -0.02 ± 0.06 percent from 35 readings of 200 seconds duration is in direct contradiction to the average change of $+2.3 \pm 0.3$ percent from 100 readings of 50 seconds duration reported by McFarlan. The individual readings in Fig. 7 are equal to or smaller than McFarlan's calculated accuracy. The balanced ionization chambers and the special circuit are chiefly responsible for this increase in accuracy. In the scattering cell used by McFarlan, the nitrobenzene was cooled by natural circulation in a comparatively small container and became so hot, by his report, that he could not apply the electric field continuously. In the readings presented here, the temperature did not increase more than about a half degree and the effect due to circulation was cancelled out by the manner of taking the readings. The important question of whether the circulation destroyed any existing "cybotatic" state is difficult to answer; apparently it had no more effect on the diffraction pattern than did increase in temperature. It is the author's opinion that the entire effect measured by McFarlan was produced by the uncontrolled circulation and temperature. The rate of natural circulation and the temperature were higher in his cell while the electric field was being applied than while it was off.

Although the spectrum of the radiation is given in Fig. 5, a better comparison between the radiation used in this work and that used by others is given by the two benzene curves in Fig. 6. The difference between the benzene diffraction pattern given by Stewart¹⁶ and the one given here is attributed to the use of a thicker scattering cell and of a less monochromatic beam of radiation to obtain the present curve. The thickness of the liquid in the scattering cell was 0.63 cm in all the tests included in this report. The secondary peak appearing at large angles agrees with the Debye¹⁷ theory of intramolecular scattering.

¹⁶ G. W. Stewart, *Phys. Rev.* **33**, 889 (1929).

¹⁷ P. Debye, *Phys. Zeits.* **31**, 419 (1930).

It has previously been observed¹⁸ for benzene and its presence explained. The benzene pattern is easily checked but it is impossible to check the intensity at the peak of the nitrobenzene diffraction pattern with the same accuracy. That this difference is not attributable to fluctuation in the x-rays is shown by the fact that the nitrobenzene diffraction pattern was taken several times between two benzene diffraction patterns during the continuous operation of the x-ray tube. The indefiniteness of the nitrobenzene peak becomes more pronounced as the temperature is lowered.

If the oxygen atoms in the nitrobenzene molecule lie in the plane of the carbon atoms and if association of the nitrobenzene molecules occurs as illustrated in Fig. 1B, the dipoles of the two associating molecules would practically cancel each other. The force exerted on the surrounding molecules by this associated pair would be very similar to the force exerted by the benzene molecule, which has no permanent moment. Consequently, the average separation of the nearest molecules in adjacent pairs should be approximately the same as for the benzene molecules. The average separation of molecules in the associated pairs should be less as a result of the greater intermolecular forces. The relation between the number of associated pairs of molecules and the total number of molecules is given by the equation presented in the introduction. The average separation between dissociated molecules should be intermediate to the other two

spacings. The peak of the nitrobenzene diffraction pattern is much lower and broader than the benzene diffraction peak. This would not be expected, considering the similarity of the molecules, unless several spacings exist between the nitrobenzene molecules. Moreover, the effect of an increase in temperature is to decrease the intensity corresponding to the smaller spacings (larger angles) and to increase the intensity intermediate to the two extreme peaks of the diffraction pattern. The agitation induced by circulating the nitrobenzene produces the same type of effect as a temperature increase. The positions of maximum change in intensity occur at larger spacings (smaller angles) as the temperature is increased. This type of change is to be expected from the change in density with temperature, but not of this magnitude. The large change in the diffraction pattern of nitrobenzene, produced by small changes in temperature, should be compared with the change for benzene. The benzene peak decreases 1 percent in height for a change in temperature of about 51°C,¹⁹ whereas the nitrobenzene peak increases 1 percent for about 17°C temperature rise.

The author feels deeply grateful to Dr. R. D. Bennett for suggesting the problem and to Professor W. C. Pierce for his helpful suggestions. He is especially indebted to Professor A. H. Compton for his interest and assistance in carrying through the project.

¹⁸ E. Rumpf, *Ann. d. Physik* **9**, 704 (1931).

¹⁹ E. W. Skinner, *Phys. Rev.* **36**, 1625 (1930).

